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Global soil characterization with VNIR diffuse reflectance spectroscopy

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Abstract

There has been growing interest in the use of diffuse infrared reflectance as a quick, inexpensive tool for soil character-ization. In studies reported to date, calibration and validation samples have been collected at either a local or regional scale. For this study, we selected 3768 samples from all 50 U.S. states and two tropical territories and an additional 416 samples from 36 different countries in Africa (125), Asia (104), the Americas (75) and Europe (112). The samples were selected from the National Soil Survey Center archives in Lincoln, NE, USA, with only one sample per pedon and a weighted random sampling to maximize compositional diversity. Applying visible and near-infrared (VNIR) diffuse reflectance spectroscopy (DRS) to air-dry soil (<2 mm) with auxiliary predictors including sand content or pH, we obtained validation root mean squared deviation (RMSD) estimates of 54 g kg^{-1} for clay, 7.9 g kg^{-1} for soil organic C (SOC), 5.6 g kg^{-1} for inorganic C (IC), 8.9 g kg^{-1} for dithionate–citrate extractable Fe (FEd), and 5.5 cmol$_c$ kg^{-1} for cation exchange capacity (CEC) with NH$_4$ at pH=7. For all of these properties, boosted regression trees (BRT) outperformed PLS regression, suggesting that this might be a preferred method for VNIR-DRS soil characterization. Using BRT, we were also able to predict ordinal clay mineralogy levels for montmoril-lonite and kaolinite, with 88% and 96%, respectively, falling within one ordinal unit of reference X-ray diffraction (XRD) values (0–5 on ordinal scale). Given the amount of information obtained in this study with ~4×10^3 samples, we anticipate that calibrations sufficient for many applications might be obtained with large but obtainable soil-spectral libraries (perhaps 10^4–10^5 samples). The use of auxiliary predictors (potentially from complementary sensors), supplemental local calibration samples and theoretical spectroscopy all have the potential to improve predictions. Our findings suggest that VNIR soil characterization has the potential to replace or augment standard soil characterization techniques where rapid and inexpensive analysis is required.
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Keywords: Diffuse reflectance spectroscopy; VNIR; PLS regression; Clay mineralogy; Boosted regression trees; Soil characterization

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1. Introduction

There is a recognized need to develop rapid and inexpensive techniques for soil characterization to support applications like quantitative soil–landscape modeling (McKenzie et al., 2000), precision agriculture (Rossel and McBratney, 1998; Thomasson et al., 2001) and global soil C monitoring (Post et al., 2001). Standard soil characterization procedures at the U.S. National Soil Survey Center cost ~$2500 per pedon with processing times of 6–12 months. As a result, relatively few locations in the United States have been fully characterized. Soil–landscape models (Hudson, 1992; Zhu et al., 2001) and soil maps have been constructed largely on the basis of field observations—including Munsell colors, hand texturing, pH indicators, and acid reaction.

Recent research has suggested that proximal visible and near-infrared (VNIR, 400–2500 nm[1]) diffuse reflectance spectroscopy (DRS) could provide inexpensive prediction of soil physical, chemical and biological properties (Ben-Dor and Banin, 1995; Reeves et al., 2000, 2002; Dunn et al., 2002; Shepherd and Walsh, 2002; Islam et al., 2003). The practical advantages of VNIR-DRS for this application include: (i) rapid scans, <1 s; (ii) a scanning area of at least 3 cm^2 which eliminates the need for fine grinding; and (iii) light-weight, portable scanners that can be used in the field as well as the lab.

The use of VNIR-DRS to characterize soils (Stoner and Baumgardner, 1981; Baumgardner et al., 1985), minerals (Hunt, 1977, 1982; Clark and Roush, 1984; Clark, 1999) and soil organic matter (SOM) (Baumgardner et al., 1985; Henderson et al., 1992) dates back to at least the 1960s. However, most of the work on soil reflectance has been focused on remote sensing applications and multispectral sensors (Baumgardner et al., 1985; Ben-Dor, 2002). Hyperspectral soil analysis, until recently, was largely descriptive and taxonomic (Stoner and Baumgardner, 1981). Recent improvements in field-portable VNIR spectroradiometers have made this technology faster, lighter, and easier to use than previously. At the same time, commercial chemometrics and data-mining software

have advanced considerably to provide a new set of tools for soil spectrometry (Friedman, 1991, 2001; Wold et al., 2001).

1.1. Fundamentals of VNIR-DRS

Spectral signatures of materials are defined by their reflectance, or absorbance, as a function of wavelength. Under controlled conditions, the signatures are due to electronic transitions of atoms and vibrational stretching and bending of structural groups of atoms that form molecules and crystals. The fundamental vibrations of most soil materials can be found in the mid-infrared region, with overtones and combinations found in the near-infrared region. For example, the fundamental features related to various components of soil organic matter generally occur in the mid-to thermal-infrared range (2.5–25 μm), but their overtones (at one half, one third, one fourth etc. of the wavelength of the fundamental feature) occur in the near-infrared (0.7–2.5 μm) region. Soil minerals such as different clay types have very distinct spectral signatures in the short-wave infrared region because of strong absorption of the overtones of SO_4^{2-}, CO_3^{2-} and OH^- and combinations of fundamental features of, for example, H_2O and CO_2 (Hunt, 1982; Clark, 1999). Electronic absorptions are primarily associated with Fe-bearing minerals (e.g., hematite, goethite, biotite, and olivine) with fundamentals found in the VNIR range (Scheinost et al., 1998, 1999) and giving rise to distinctive colors long employed in the field characterization of soils (Schwertmann, 1993).

VNIR soil reflectance is a function of soil composition—organic materials, primary minerals, clay minerals, salts, and poorly-crystalline andic materials—which is central to the U.S. Soil Taxonomy system and soil management interpretations (Table 1). VNIR reflectance spectra for most primary and secondary minerals have been well-described, though quartz and feldspars have weak to non-existent absorptions in the VNIR range (Hunt, 1977, 1982; Clark, 1999; Clark et al., 2003). The VNIR spectra for andic materials, vermiculites and (surprisingly) SOM have not been well described, perhaps due to the complexity or vague definitions of these materials. In addition to measuring mineral and organic soil constituents, VNIR-DRS has been used to estimate

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[1] In remote sensing terminology, 400–2500 includes the Visible (VIS), Near-Infrared (NIR), and Short-Wave Infrared (SWIR) regions.

Table 1
Soil constituents with established VNIR-DRS absorptions and related soil taxonomy diagnostics

Key soil constituents	VNIR absorptions	Soil taxonomy diagnostics
SOM	C–H, N–H, C–O	Histic, folistic, mollic, umbric, sombric, melanic, spodichorizons; fibric, hemic, sapric, limnic materials
$CaCO_3$, $CaSO_4 \cdot H_2O$	CO_3, SO_4	Calcic, petrocalcic, gypsic, petrogypsic
Clay minerals	H_2O, O–H, Fe	Argillic, natric, glossic, oxic, kandic, coefficient of linear extensibility (COLE)
Fe-oxyhydroxides	Electronic absorptions	Oxic, spodic, ortstein, plinthite, placic, redoximorphic features
Mafic primary minerals	Electronic absorptions	Weatherable primary minerals
Poorly-crystalline materials	?C–O, C–H, N–H, H_2O, O–H?	Melanic, andic soil materials

fertility measures such as CEC, base saturation, pH, exchangeable bases and extractable P (Ben-Dor and Banin, 1995; Dunn et al., 2002; Shepherd and Walsh, 2002; Islam et al., 2003), texture (Ben-Dor and Banin, 1995; Shepherd and Walsh, 2002; Cozzolino and Moron, 2003; Islam et al., 2003; Moron and Cozzolino, 2003), extractable Fe (Ben-Dor and Banin, 1995; Dunn et al., 2002), and total elements Ca, Mg, Fe, Mn, K, and Cu (Cozzolino and Moron, 2003; Moron and Cozzolino, 2003; Udelhoven et al., 2003). To the extent that secondary properties can be related to soil composition (e.g., CEC to clay mineralogy and SOM) we would expect to find robust, global relationships with VNIR-DRS.

1.2. Modeling approaches

1.2.1. Boosted regression trees

Following Friedman (2001), boosted models can be expressed in the general form:

$$F\left(x; \{\beta_m, a_m\}_0^M\right) = \sum_{m=0}^{M} \beta_m h(x; a_m) \quad (1)$$

where $h(x; a)$ represents a simple classification function or "base learner" with parameters a and input variables x, m represents the model step, and β_m is a weighting coefficient for step m. With the well-known AdaBoost algorithm of Freund and Schapire (1997), the base learner is applied sequentially to reweighted calibration datasets such that observations with larger residuals receive proportionally greater weights in subsequent iterations. The final classification is computed with a weighted vote as shown in (1). Friedman (2001, 2002) has developed a new approach to fitting

additive models of the form shown in (1), termed a Gradient Boosting Machine (GBM). With this approach, a numerical solution is found that involves sequentially fitting the base learner (using least squares) to "pseudo"-residuals computed from the gradient of a differentiable, prescribed loss function (lack of fit)—with respect to the predicted value for each calibration observation for the current step. In a further development, Friedman (2002) has found that the use of "bagging" or random subsampling from the calibration set in conjunction with boosting improves on boosting alone.

For this application, we used Boosted Regression Trees (BRT) which essentially adds boosting to a regression tree routine like CART® (Breiman et al., 1983). Though we used the commercial software Treenet® for this project, a BRT module has recently become available in the R freeware statistical package which should make this modeling approach more widely available. The primary advantages of BRT include (i) the ability to include a large number of weak relationships in a predictive model; (ii) insensitivity to outliers in the calibration dataset; (iii) the elimination of the need for uniform data transformations; and (iv) relative immunity to "overfitting" (Freund and Schapire, 1997, 2000; Friedman et al., 2000a,b; Ridgeway, 2000; Friedman and Meulman, 2003). Friedman et al. (2000a) has also demonstrated the links between boosting (a machine learning algorithm) and maximum-likelihood, additive modeling in statistics. Given the high-dimensional nature of diffuse reflectance spectroscopy and the large number of weak and contingent relationships between soil composition and VNIR reflectance, BRT would seem to be an ideal tool for VNIR-DRS soil characterization.

1.2.2. PLS regression

For soil characterization, Partial Least Squares (PLS) regression using the 1st derivatives of soil reflectance is commonly used to reduce high-dimensional spectral data obtained from NIR detectors (Reeves et al., 1999; Dunn et al., 2002; Martin et al., 2002; McCarty et al., 2002; Cozzolino and Moron, 2003; Moron and Cozzolino, 2003; Udelhoven et al., 2003). PLS regression, a "chemometric" technique, is similar to Principle Components Regression (PCR) in that both employ statistical rotations to overcome the problem of high-dimensional, correlated predictors, except that in PLS the X and Y variables are rotated relative to the response variables to maximize predictive power (Geladi and Kowalski, 1986; Wold et al., 2001).

These "empirical" modeling approaches have commonly been applied to one or more field studies, with local calibration data required for each application. There have been a few regional calibrations reported in the literature (Dunn et al., 2002; McCarty et al., 2002; Shepherd and Walsh, 2002), though in the one temperate region study (McCarty et al., 2002) there are questions as to whether validation has been sufficiently independent (Brown et al., in press). A key limitation for "black box" empirical modeling is that results cannot be reliably extended beyond the range of materials used in the calibration phase (Dardenne et al., 2000). Shepherd and Walsh (2002) have proposed that spectral libraries be constructed with associated lab calibration data, and that these libraries be used to predict soil properties for new samples that have been screened for spectral similarity. Spectrally dissimilar soils are submitted to the lab for characterization with subsequent inclusion in an expanded spectral library. In such a manner a global spectral library could be constructed, though the number of calibration samples required for such a library has not been estimated, nor have precise rules been established for determining sufficient spectral similarity for reliable prediction.

1.3. Study objectives

Our primary objective in this study was to evaluate the precision and accuracy of empirical VNIR soil characterization modeling when applied to a large, diverse, "global" set of *independent* soil samples.

We use the term "global" in this context to emphasize sample independence, a complete range of sample depths, and the wide range of climatic regions included in the spectral library. Though samples from five continents were included in this study, the majority came from the U.S. and associated territories. Secondly, we compared BRT data-mining and PLS regression with and without auxiliary predictors. Finally, we estimated the number of calibration samples required to construct a truly global, empirical, VNIR-DRS soil characterization model.

2. Methodology

2.1. Sampling design

We obtained laboratory characterization data for all profiles sampled from 1988 to 1999 and subsequently characterized by the US National Soil Survey Center-Soil Survey Laboratory (NSSC-SSL) in Lincoln, NE; a total of 55,962 samples from across the United States as well as Africa and Asia. Samples with missing data for $CaCO_3\%$ equivalent and pH (1:1 in H_2O) ≥ 7.6 were removed from the dataset to reduce potential problems with unmeasured Inorganic C. We then selected 46,363 samples for which the following soil characterization values were available, with NSSC-SSL method codes provided in parentheses (Soil Survey Staff, 1996): (i) IC by HCl treatment and manometer (6E1); (ii) SOC by modified Walkley–Black (6A1) or Total C by combustion (6A2); (iii) pH, 1:1 in H_2O and 2:1 in 0.01 M $CaCl_2$ (8C1f); (iv) CEC using NH_4OAc at pH 7.0 (5A1); (v) exchangeable sodium percentage (ESP) using NH_4OAc at pH 7.0 (5D2); (vi) clay % and sand % via the pipette method (3A1); (vii) 15-bar H_2O retention per unit clay (8D1); and (vii) CEC per unit clay (8D1). In addition to these composite soil properties, we also screened to only include samples with mineralogical characterization, either (i) clay mineralogy as determined by XRD on oriented clays with results recorded in relative peak intensities with ordinal values of 0–5 (we converted NSSC-SSL values of 6, indicating no peak, to 0 for ordinal consistency) (7A2); or (ii) optical mineralogy for fine sand fractions (7B1).

The parameters listed above were transformed using Principal Components Analysis (PCA), with

standardized and centered variables. We then stratified the samples using the *clara* clustering routine in R which approximates Partitioning Around Mediods for large datasets (Kaufman and Rousseeuw, 1990), with 20 subsets of 2000 each, and $k = 12$ clusters. The clusters were ranked according to size (cluster with the least number of samples was ranked 12), a random number (0–1) was generated for each sample, and a weighting factor was computed as: cluster rank $\times$ random (0–1). The data were subsequently sorted by pedon and the inverse of the weighting factor. The first sample for each pedon in this sorted dataset was selected as the primary sample, and the second as the alternate to be selected in situations where the primary could not be found in the archive.

Through this process, a total of 4184 compositionally diverse, well-characterized, and largely independent soil samples were selected for this study. Of the total, 3760 samples came from the US, with 416 samples from 36 different countries in Africa, Asia, S. America and Europe (8 samples had no location information). Within the US, samples were obtained from all 50 states and two territories (Northern Mariana Islands and Puerto Rico), with the number of samples per state ranging from 2 (South Carolina) to 254 (Texas). A total of 628 US counties and administrative districts were included with a maximum of 43 samples taken from any one county. Major horizon designations included 5 O, 1106 A, 70 E, 2412 B, 518 C and 4 R horizons with 69 miscellaneous materials. Almost every type of mineral measured by the NSSC-SSL was represented in the selected soil samples.

2.2. Spectral scanning and processing

We scanned both air-dry and oven-dried (105 °C) crushed (<2 mm) subsamples for each of the soil samples using an ASD "Fieldspec Pro FR" VNIR spectroradiometer (Analytical Spectral Devices, Boulder, CO) with a spectral range of 350–2500 nm, 2 nm sampling resolution and spectral resolution of 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. Soils were scanned from below using a high-intensity source probe (Analytical Spectral Devices, Boulder, CO) and white light source with Duraplan® borosilicate optical-glass Petri dishes to hold samples and a Spectralon® panel for white referencing. Two composite scans (consisting of 15 internally averaged

scans of 100 ms each) were obtained for each sample, with a 90° sample rotation between scans. Scans of oven-dried samples provided no discernable improvement over air-dried scans either separately or in combination, therefore only air-dried results are reported.

The wavelength-dependent signal-to-noise ratio (S/N) for our instrument was estimated by taking repeated irradiance measurements of a Spectralon® white-reference panel over a 5 minute interval and repeating this exercise five times over a week (Fig. 1). For pure kaolinite, $CaCO_3$ and a few selected soil samples, we then fit cubic smoothing splines using the "smooth.spline" function in R (R Development Core Team, 2004) with wavelength-dependent weights equal to $(S/N)^2 \approx$ (error variance)$^{-1}$ for reflectance measurements. The knot spacing and spline tension were adjusted heuristically until a fit with 5 nm knot-spacing and a smoothing parameter of 0.05 was found to smooth "noise" yet retain known absorption features.

Replicate soil scans were compared (reflectance and 1st derivatives) to check for errors, then averaged to produce a single reflectance scan for each sample. Using the weights and smoothing parameters described above, cubic smoothing splines were fit to each raw spectral curve with 1st derivative values extracted at 10 nm intervals from 360 to 2490 nm.

2.3. Modeling and fit assessment

A commercial BRT package, Treenet® 1.0 (Salford Systems, San Diego, CA, USA), was employed in this
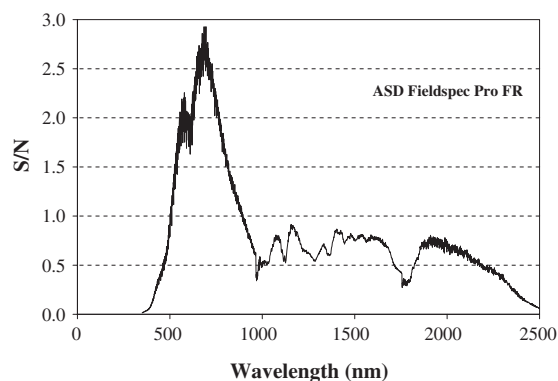

Fig. 1. Wavelength-specific signal-to-noise (S/N) ratio for ASD Fieldspec Pro FR spectroradiometer used in study.

Table 2
Reflectance variables and soil characterization parameters determined on <2 mm size fraction following standard soil survey procedures (Soil Survey Staff, 1996)

Parameter	Units	Definition
CEC	$cmol_c\ kg^{-1}$	CEC by NH_4OAC is the cation exchange capacity of the sample, determined by 1N NH_4OAC in a system highly buffered at pH 7.0
CLAY	$g\ kg^{-1}$	Total clay is the soil separate with <0.002 mm particle diameter, including clay-size carbonate. Pipette method
D1		1st derivative of VNIR spectral curve at 10 nm intervals, 360–2490 nm
FEd	$g\ kg^{-1}$	Dithionite citrate extractable Fe, considered a general measure of total pedogenic iron
IC	$g\ kg^{-1}$	Inorganic C in the <2 mm fraction measured by CO_2 evolution after acid treatment using pressure–calcimeter method
KK	Ordinal	Relative XRD peak intensity of kaolinite (0–5)
PH		The pH of a sample measured in 0.01 M $CaCl_2$ at a 1:2 soil:solution ratio
MT	Ordinal	Relative XRD peak intensity of montmorillonite (0–5)
SOC	$g\ kg^{-1}$	Chemically oxidizable soil organic C as determined by Walkley–Black method
SND	$g\ kg^{-1}$	Total sand is the soil separate with 0.05 to 2.0 mm particle diameter, measured by pipette method
TC	$g\ kg^{-1}$	Total carbon as determined by combustion

study. The commercial PLS package Unscrambler 8.0.5 (CAMO Technologies, Inc., Woodbridge, NJ, USA) was used in selected cases for comparison. For all modeling, extreme observations (never more than one per variable of interest) were removed a priori and hold-out 1/6th cross-validation was used to estimate predictive accuracy. A key requirement for model validation is that the validation samples be "independent"-collected from different locations, at different times and preferably even scanned with different spectroradiometers (Brown et al., in press). While we were not able logistically to accomplish the last requirement, the samples used in this study were otherwise independent. Therefore in this situation, cross-validation *is* independent validation.

For Treenet® modeling, a maximum of 12 branches/node were used, and a 20% random test set taken from the first calibration set (5/6 of available observations) was used to estimate the optimum number of trees for each target variable—rounded up to the nearest 10 trees, to a maximum of 300 trees (ordinal mineralogy) or 1000 trees (continuous soil properties). In general, increasing the number of trees in a model almost always improved cross-validation statistics, but increasing trees came at the cost of increasing computational requirements and at the imposed limits incremental improvements were negligible. For PLS regression modeling (soil properties only), the optimum number of components (j) to include in the model was determined by examining the cross-validation results and identifying the first point at which $\sigma_j < \min(\sigma_{j+1}, \sigma_{j+2})$ up to a maximum of 50 components. PLS component selection should ideally be based upon calibration data alone (as we did with BRT tree selection), so the results reported from PLS modeling are slightly optimistic.

Codes for the key soil and spectral variables used are provided in Table 2.

2.3.1. Mineralogy

The most abundant clay minerals, in decreasing order kaolinite (KK), montmorillonite (MT) and vermiculite, were modeled using the Treenet® classification mode which assigns probabilities to potential output classes—with XRD clay mineralogy available for a total of 3372 samples. To impose an ordinal structure on the classification probabilities, we used a linear cost matrix shown in Table 3 to compute penalties for misclassification. So the penalty value

Table 3
Misclassification cost matrix used to impose ordinal relationships on Treenet® classification modeling for XRD clay mineralogy

XRD	VNIR					
	0	1	2	3	4	5
0	0	1	2	3	4	5
1	1	0	1	2	3	4
2	2	1	0	1	2	3
3	3	2	1	0	1	2
4	4	3	2	1	0	1
5	5	4	3	2	1	0

Shaded cells indicate VNIR prediction=lab measure.

(cost of being wrong) is computed as a sum of weighted probabilities, for example:

$$\text{Penalty}(1) = p(0) \times 1 + p(1) \times 0 + p(2) \times 1 + p(3)$$
$$\times 2 + p(4) \times 3 + p(5) \times 4.$$

The predicted output for a given sample is simply the ordinal value with the *lowest* penalty value. To evaluate ordinal model results we computed kappa coefficients (κ) (Thompson and Walter, 1988; Agresti, 1996) with linear weighting to match the cost structure employed in model construction (Table 3).

2.3.2. Composite soil properties

Using Treenet® in regression mode, we first targeted all composite soil properties available (Section 2.1). Within this set of variables, we were able to construct effective models for CLAY, CEC, SOC, IC, and FEd (Table 2). Total C by dry combustion (TC) was only available for a fraction of the dataset—not sufficient for calibration requirements—so to maintain consistency we only modeled the 3794 samples with SOC (Walkley–Black). We also fit VNIR models with % sand (SND) and pH in CaCl$_2$ (PH), as auxiliary predictors to estimate the additional predictive value provided by these relatively easy to measure parameters (pH in CaCl$_2$ proved a better auxiliary predictor than pH in H$_2$O). For comparison, we fit PLS regression models for the same target variables, with and without the auxiliary SND and PH predictors.

The following statistics were computed to evaluate the quality of model fits following Gauch et al. (2003):

$$\text{MSD} = \sum_n \left(Y_{pred} - Y_{meas} \right)^2 / N \qquad (2)$$

$$\text{RMSD} = \sqrt{\text{MSD}} \qquad (3)$$

$$\text{Bias} = \sum_n \left(Y_{pred} - Y_{meas} \right) / N \qquad (4)$$

$$\text{SB} = \text{Bias}^2 \qquad (5)$$

$$\text{NU} = (1 - b)^2 \times \text{var}(Y_{meas}) \qquad (6)$$

$$\text{LC} = (1 - r^2) \times \text{var}(Y_{pred}) \qquad (7)$$

where b and r^2 are the slope and coefficient of determination, respectively from the least-squares regression of Y_{pred} on Y_{meas}. The Mean Squared Deviation (MSD) is partitioned into three independent components describing lack of accuracy due to bias (SB), non-unity regression line (NU), and lack of correlation (LC), with MSD = SB + NU + LC.

2.3.3. Assessment lab accuracy and precision for soil C

Out of the 4184 independent samples selected for this study, we selected all samples with both SOC (Walkley–Black) and TC-IC data available for a comparison of two standard analytical methods. These samples were broken into 10 strata by IC and SOC using K-means clustering (Hartigan and Wong, 1979) in R (R Development Core Team, 2004). A total of 20 samples were randomly selected from each strata (200 total) for independent laboratory determination at Montana State University (MSU) of Total C (TC) by dry combustion using a LECO C/N/S 2000 analyzer (LECO Corporation, St. Joseph, MI, USA). Inorganic C (IC) was determined using a modified pressure calcimeter method (Sherrod et al., 2002).

3. Results

3.1. Clay mineralogy

The results of BRT mineralogical modeling are presented in Tables 4 and 5. For Kaolinite (KK), we obtained κ(linear weighting)=0.62, with 62% of

Table 4
Correspondence table displaying ordinal "peak intensity" kaolinite (KK) values as measured using XRD and predicted using VNIR and Treenet® with 1/6th cross-validation; κ(linear weighting)=0.62 for validation (N=3372) and κ=0.94 for calibration (N=16,860)

XRD	VNIR						Row totals
	0	1	2	3	4	5	
0	74	73	20	8	1	1	177
1	26	319	154	15	0	0	514
2	11	160	986	265	8	1	1431
3	3	29	293	568	46	10	949
4	0	0	12	70	68	24	174
5	0	0	1	10	32	84	127
Col. Totals	114	581	1466	936	155	120	3372

Shaded cells indicate VNIR prediction=lab measure.

Table 5
Correspondence table displaying ordinal "peak intensity" montmorillonite (MT) values as measured using XRD and predicted using VNIR and Treenet® with 1/6th cross-validation; κ(linear weighting)=0.64 for validation (N=3372) and κ=0.90 for calibration (N=16,860)

XRD	VNIR						Row totals
	0	1	2	3	4	5	
0	850	131	182	53	9	0	1225
1	80	53	81	29	0	0	243
2	39	58	267	156	5	0	525
3	23	18	237	574	124	0	976
4	3	1	25	185	158	0	372
5	0	0	0	10	21	0	31
Col. Totals	995	261	792	1007	317	0	3372

Shaded cells indicate VNIR prediction=lab measure.

observations having an exact match between XRD and VNIR and 96% having VNIR predicted values within one ordinal class of XRD values. For montmorillonite, we obtained κ(linear weighting)=0.64, with 56% of observations having an exact match between XRD and VNIR and 88% having VNIR predicted values within one ordinal class of XRD values. For Vermiculite (not shown), we obtained κ(linear weighting)=0.40, with 53% of observations having an exact match between XRD and VNIR and 83% having VNIR predicted values within one ordinal class of XRD values. Only 40% of samples had detectable amounts of vermiculite clays and only 24 samples had a peak intensity >3, which proved insufficient for Treenet® calibration requirements. It should be noted that κ(kappa coefficient of agreement) values are specific to a given data distribution and cannot be directly compared across different datasets.

Given the inherent difficulty of obtaining consistent peak values using XRD analysis (Whittig and Allardice, 1986), we would not have perfect agree-

ment even if samples were re-analyzed at the NSSC-SSL using identical equipment and operator. Were samples to be analyzed by different operators, using different equipment and in a different laboratory, the disagreement could become quite large. In fact, it is not clear how the NSSC-SSL XRD determination procedures could be replicated at outside laboratories short of having personnel trained directly at the Lincoln, NE facility. The VNIR mineralogy results, for KK and MT at least, might not be far removed in precision from XRD replication in an independent lab.

3.2. Composite soil properties

3.2.1. Summary of soil properties

Summary statistics for key soil characteristics are provided in Table 6. The data include a full range of textures for all 4184 samples and PH ranging from 2.56 to 10.75. The IC data is highly skewed with over half of the samples having no measured carbonates and relatively few samples having significant amounts up to 128.8 g kg^{-1}. There was one extreme and potentially influential SOC value at 536.8 g kg^{-1}, with the next largest recorded value at 241.6 g kg^{-1}. Similarly the largest CEC value was 165.5 cmol$_c$ kg^{-1} followed by 106.5 cmol$_c$ kg^{-1} and the largest FEd value was 236 g kg^{-1} followed by 158 g kg^{-1}. These three extreme values were removed prior to BRT and PLS cross-validation modeling.

3.2.2. General results

Several results were observed for all targeted soil properties (Table 7).

- A lack of correlation (LC) made by far the largest contribution to lack of fit (MSD) for all models. As indicated by bias and squared bias (SB) statistics, bias made a negligible contribution to the overall

Table 6
Summary statistics for key soil parameters

	CLAY g kg^{-1}	CEC cmol$_c$ kg^{-1}	IC g kg^{-1}	SOC g kg^{-1}	FEd g kg^{-1}	SND g kg^{-1}	PH
Min.	1	0.2	0.0	0.0	0	1	2.56
1st quart.	109	8.9	0.0	1.9	7	134	4.80
Median	226	15.7	0.0	4.7	12	333	6.02
3rd quart.	366	25.9	1.6	12.3	20	571	7.49
Max	930	165.5	128.8	536.8	236	994	10.75
N	4184	4184	4184	3794	2910	4184	4184

Table 7

Soil property predictions using 1st derivative reflectance (D1) of air-dry, sieved (<2 mm) soil samples with either % sand (SND) or PH ($CaCl_2$ solution) as auxiliary predictors

Target	CLAY (g kg^{-1})		CEC (cmol$_c$ kg^{-1})[a]		SOC (g kg^{-1})[b]		IC (g kg^{-1})		FEd (g kg^{-1})[c]	
Predictors	D1	D1+SND	D1	D1+SND	D1	D1+SND	D1	D1+PH	D1	D1+SND
#trees	1000	1000	1000	1000	1000	1000	900	1000	1000	1000
N	4184	4184	4183	4183	3793	3793	4184	4184	2909	2909
BRT (Treenet®), 1/6th cross validation										
RMSD	95	54	6.7	5.5	9.0	7.9	6.2	5.6	9.6	8.9
Bias	−2	−1	−0.1	−0.2	−0.3	−0.4	−0.4	−0.3	−0.4	−0.5
MSD	8940	2954	45	30	81	62	39	31	92	80
SB	3	1	0	0	0	0	0	0	0	0
NU	2884	382	14	8	25	19	10	7	37	31
LC	6053	2572	31	22	56	42	29	24	54	48
r^2	0.73	0.91	0.74	0.83	0.82	0.87	0.83	0.86	0.73	0.77
Slope	0.70	0.89	0.72	0.79	0.76	0.79	0.78	0.82	0.67	0.69
Comparison RMSD values										
BRT, calibration	38	23	2.8	2.8	4.1	4.0	3.5	2.9	4.8	4.9
PLS, cross-valid.	108	72	8.9	7.1	12.7	12.2	7.1	7.0	12.0	11.5

[a] An extreme value of CEC=165.5 cmol$_c$ kg^{-1} was removed from the analysis.

[b] An extreme value of SOC=536.8 g kg^{-1} was removed from the analysis.

[c] An extreme value of FEd=236 g kg^{-1} was removed from the analysis.

lack of cross-validation fit (in all cases <0.5% of MSD). BRT models tended to underestimate for high soil property values as indicated by regression slope values <1 and non-unity (NU) values averaging 30% of MSD. Some of this underestimation could be due to the relative paucity of observations available at the higher ends of the property scales.

- The use of auxiliary predictors—either sand content (SND) or pH in $CaCl_2$ (PH)—improved cross-validation predictions for all soil properties modeled.
- Calibration RMSD values for all models were far below validation RMSD with calibration MSD 17–31% of validation MSD. This indicates that the ~4000 samples used for calibration in this study, while larger than any previously published spectral library, represent only a fraction of the total calibration samples required for optimum empirical VNIR soil characterization.
- In every model reported, Boosted Regression Trees (BRT) provided notably improved validation RMSD statistics relative to PLS regression (Table 7). This is not surprising given the non-linear and contingent relationships between VNIR reflectance and soil composition (Clark, 1999). Boosted Regression Trees can incorporate complex, non-linear

relationships and interactions whereas PLS regression is built upon linear relationships between predictors and the target variable of interest.

3.2.3. Validation results for specific properties

We had difficulty predicting CLAY based upon VNIR alone. Referring to Table 7, we can see that the BRT model yielded a RMSD of 95 g kg^{-1} (9.5%), not acceptable for most applications. Including SND as a predictor dropped the RMSD to 54 g kg^{-1}, with 91% of the CLAY variability explained. The regression slope also increased from 0.70 to 0.89 through the inclusion of SND as a predictor. A plot of VNIR+SND-predicted CLAY vs. pipette-CLAY is provided in Fig. 2a, showing the vast majority of predictions falling within ±10% of the reference data, little evidence of residual heteroscedasticity, and considerably fewer samples with >60% CLAY. (Predicting CLAY using SND alone explained very little of the variability.) Not shown, we also modeled SND using VNIR 1st derivatives, but obtained a weak fit with r^2=0.57 and RMSD=176 g kg^{-1}.

As with the CLAY models, CEC prediction was significantly improved with the addition of SND as a predictor (RMSD improved from 7.1 to 5.5 cmol$_c$ kg^{-1}
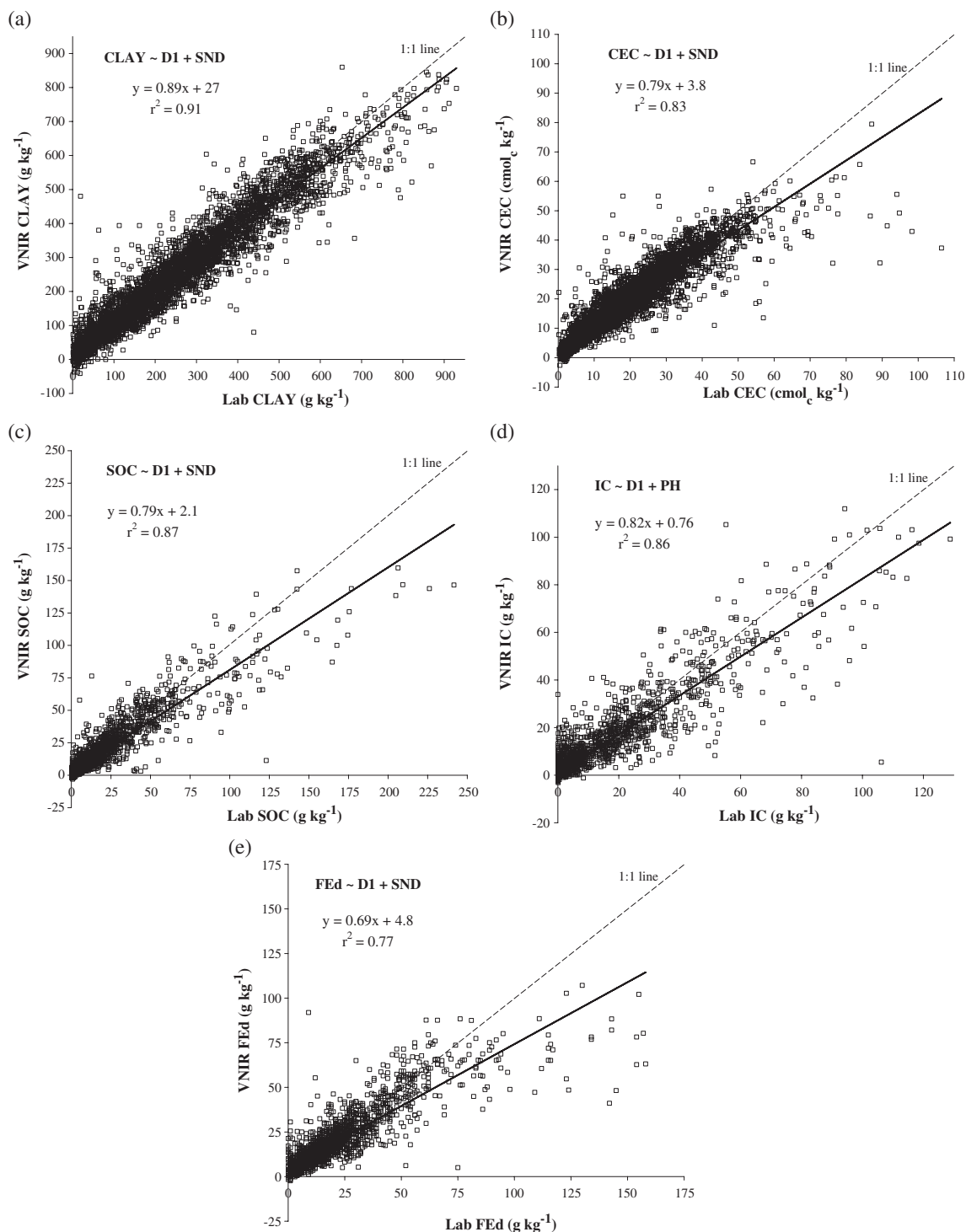
Fig. 2. Predicted vs. measured (a) clay content (pipette method); (b) CEC (NH_4 at pH=7); (c) SOC (Walkley–Black); (d) IC (electronic manometer); (e) FEd (dithionite–citrate extraction) with 1/6th cross-validation using air-dry, 1st derivative VNIR reflectance spectra, Treenet®, and either sand content or pH ($CaCl_2$) as an auxiliary predictor.

with the inclusion of SND as shown in Table 7). However, the improvement was not as dramatic even with SND included, $r^2 = 0.83$ with a regression slope of 0.79. There were only a few observations with $CEC > 60$ $cmol_c$ kg^{-1} which contributed to the under prediction of high CEC values (Fig. 2b). Though related to clay content, mineralogy and organic composition, CEC is measured in the laboratory as a chemical property only indirectly related to VNIR reflectance.

We found it difficult to predict SOC with the precision required for most applications, even with SND included as an auxiliary predictor (Table 7). With the 1st derivative of VNIR (D1) alone, the RMSD was 9.0 g kg^{-1} (0.9% C) and this only decreased to 7.9 g kg^{-1} ($r^2 = 0.87$) with the inclusion of SND. Fig. 2c shows significant scatter even at low SOC values, with wide scatter and under prediction at $SOC > 75$ g kg^{-1} (7.5%). Even the calibration RMSD values were at ~4 g kg^{-1}, which might not be acceptable for some applications.

Surprisingly, using PH as a predictor in addition to reflectance did not markedly improve IC predic-

tion (Table 7). The RMSD for D1+PH was computed as 5.6 g kg^{-1}, with an RMSD estimate of 6.2 g kg^{-1} for reflectance alone ($r^2 = 0.83$ and 0.86, respectively). Looking at a plot of VNIR vs. lab IC (Fig. 2d), we can see a considerable amount of scatter even for samples with no measured IC. The BRT models did under-predict high measured IC values (slope = 0.81–0.86), but the total contribution to error as indicated by NU was relatively small— most of the samples had little to no measured IC. In the construction of this dataset, $CaCO_3(eq) = $"NA" were converted to zero since all samples are screened for the presence of carbonates and then submitted for $CaCO_3(eq)$ determination only if necessary. However, small amounts of $CaCO_3$ might not always be detected. Our model could also require a larger number of samples with detectable IC for robust calibration.

We had the greatest difficulty in predicting citrate–dithionite extractable Fe (FEd) using 1st derivative VNIR reflectance (D1), with RMSD = 9.6 and $r^2 = 0.73$. The inclusion of SND yielded only a very
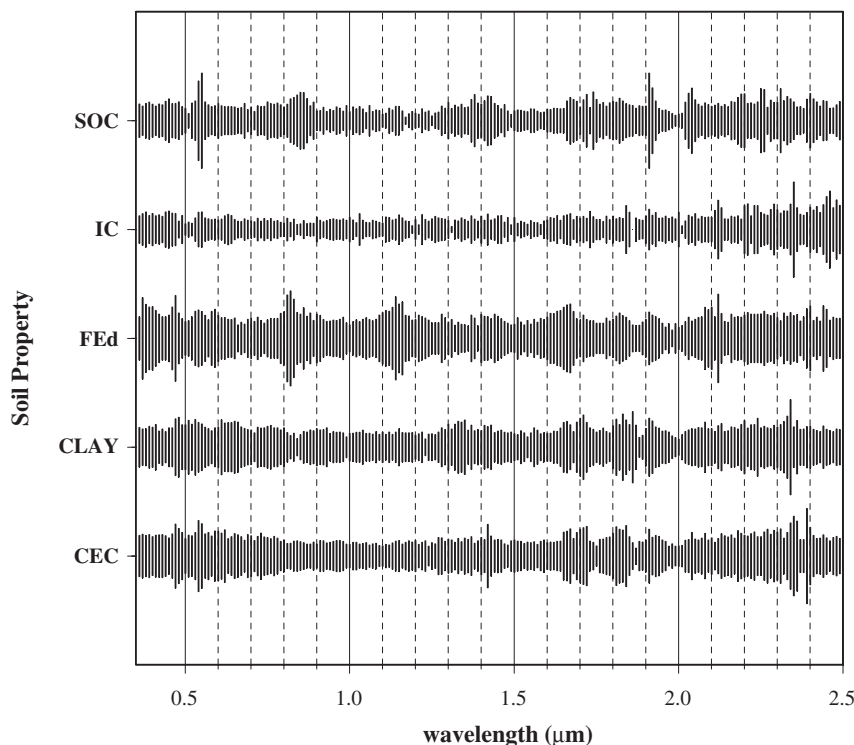

Fig. 3. Relative wavelength importance for Treenet® soil characterization models.

slight improvement with RMSD = 8.9 and $r^2 = 0.77$. Most of the error in the BTR models was due to a lack of correlation and under prediction at higher values (see LC, NU and MSD values in Table 7). Even with SND included as a predictor, the models under-predicted for high FEd measured values (see Fig. 2e). As with IC, there were many samples clustered near zero and relatively few samples with significant amounts of the targeted material (for FEd we only had 2909 samples total).

3.3. Important wavelengths

With Treenet® it is possible to estimate the relative importance of model predictors, or in this case VNIR 1st derivative wavelengths (Fig. 3). For SOC, visible wavelengths of 0.54 and 0.55 μm are noticeably important as well as the 1.91 μm H_2O band. But the SOC model also depends upon a substantial amount of information in the 2.0–2.5 μm range, due to both M–OH and various C–O and C–H absorptions. The region
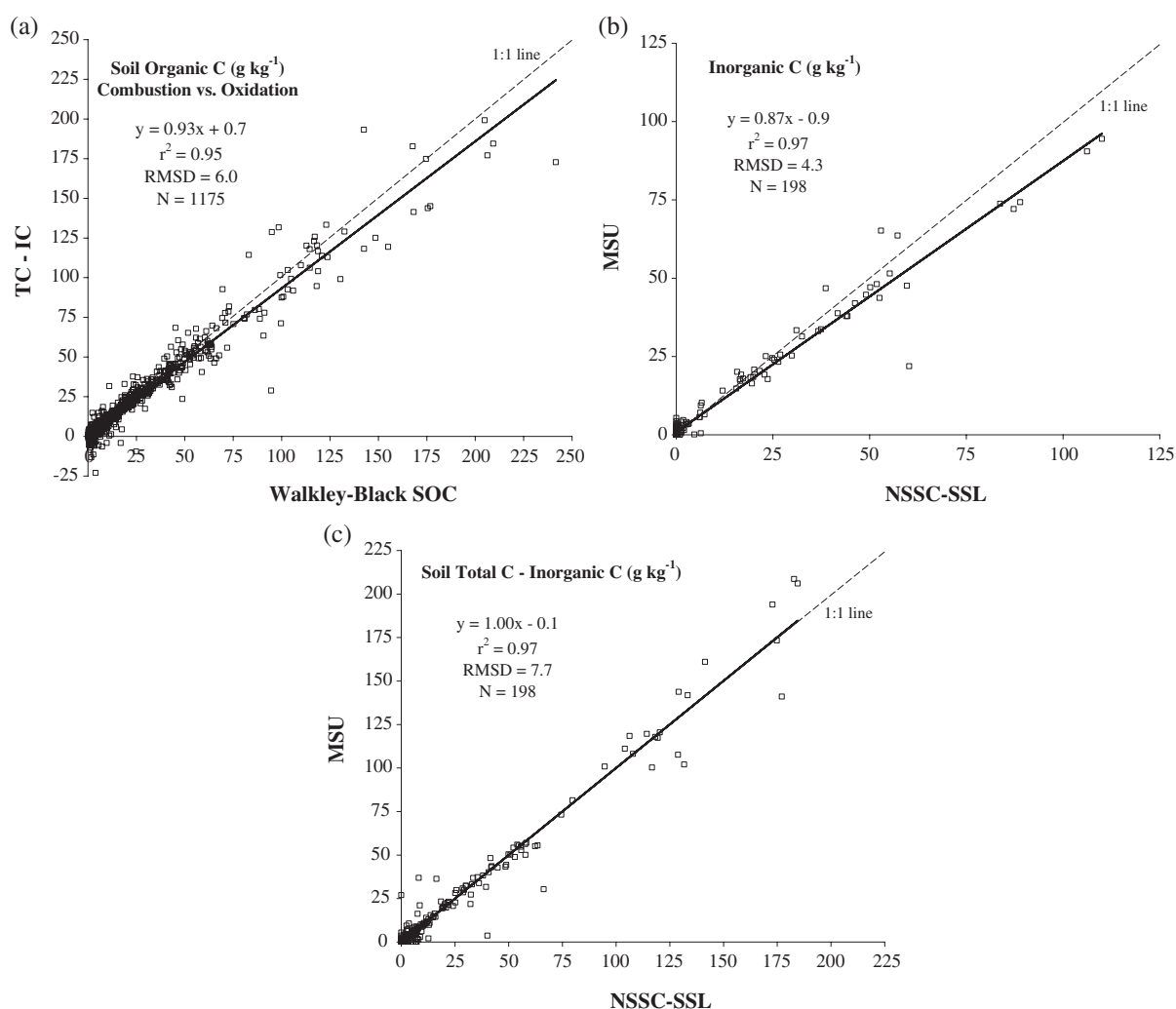

Fig. 4. Accuracy and precision of soil C analytical measurements as indicated by: (a) SOC (Walkley–Black) vs. (Total C–Inorganic C) for 9687 samples extracted from the NSSC-SSL database with both measures available; (b) Inorganic C as determined at Montana State University (modified pressure calcimeter) vs. NSSC-SSL (electronic manometer); and (c) Total C–Inorganic C as determined at Montana State University vs. NSSC-SSL.

of the C–H stretch overtone ~1.7 μm is also important. For IC, the most important band is at the well-documented 2.35 μm CO_3 absorption and with information also obtained at the leading edge of the 2.5 μm CO_3 feature. For FEd, CLAY and CEC, information is obtained from throughout the VNIR range. Some of these wavelengths can be related to electronic absorptions, metal–OH bends, the OH stretch, etc…. However, given the multitude of overlapping absorptions in the VNIR range and the number of wavelengths making significant contributions to the BRT models, it quickly becomes difficult to identify particular spectral features with confidence (Hunt, 1977; Clark et al., 1990, Clark, 1999; Ben-Dor et al., 1999). There also appears to be much redundancy in the spectra in the sense that if some bands are deleted other bands can often serve as surrogates with little or no loss in prediction accuracy.

3.4. Laboratory soil C determination

SOC as determined by the "Walkley–Black" method (Walkley and Black, 1934) is only loosely correlated with SOC as determined by dry combustion Total C less Inorganic C. Fig. 4a shows a very "fuzzy" correlation between these two standard methods with a deviation from the 1 : 1 line at higher SOC values. In terms of the sum of squared error, a lack of correlation (LC) and the non-unity regression line (NU) account for 87% and 12% of MSD, respectively. The RMSD value of 6.0 g kg^{-1} is comparable to estimated RMSD values between VNIR models and SOC (Walkley–Black).

Even when we replicated dry combustion Total C (TC) determination and Inorganic C (IC) via electronic manometer for a representative subset, MSU data did not match NSSC-SSL data as closely as we anticipated. RMSD for the between-lab IC comparison (Fig. 4b) was estimated at 4.3 g kg^{-1} with two outliers removed. For TC-IC (which combines the errors of two measurements), RMSD was estimated at 7.7 g kg^{-1} (or ~0.8%) with 2 outliers removed (Fig. 4c). Cast in this light, our VNIR models for SOC and IC prediction are not far removed from what might be obtained by re-analyzing NSSC-SSL samples in an independent lab. (Using 20% replication, we estimated *internal* MSU measurement error at 1.4 and 3.7 g kg^{-1} for IC and TC, respectively.) Sample handling and coding errors are part of life in any

analytical laboratory, measurement errors are not insignificant, and between-laboratory comparisons often reveal surprising discrepancies. Precision and accuracy are elusive goals in soil characterization and yet are not often quantified—for both VNIR and standard laboratory methods.

4. Discussion

4.1. BRT vs. PLS regression

While almost all important soil constituents have characteristic VNIR reflectance curves, absorption features are rarely unique to a given property. This is why BRT modeling—which can incorporate multiple, high-level interactions as well as linear and non-linear correlations—is such a powerful and appropriate technique for VNIR-DRS soil characterization. In a sense, BRT modeling is an empirical approach that mimics what workers like Clark et al. (2003) have accomplished with continuum-removal and an expert system with deductively constructed interactions and contingencies. PLS regression, which clearly did not perform as well in this application, can be used primarily to model linear correlations and is suited to small data sets, but has no fundamental capability to identify interactions or fit non-linear relationships. In the MIR (Mid-Infrared) range, where absorption features are more clearly separated, PLS regression might suffice but for VNIR-DRS we found boosted regression trees to be a superior modeling approach.

4.2. Appropriate target parameters

In addition to modeling clay mineralogy, we developed models to predict composite soil properties like clay, CEC and FEd. But the clay-size fraction in soils is actually comprised of a number of different minerals including materials like calcite and dolomite which have very different spectra than secondary phyllosilicates. CEC is related to mineral composition and organic matter, but the exact nature of that relationship is complex and the use of CEC is only appropriate within a certain pH range (e.g., for acidic soils, Effective Cation Exchange Capacity or ECEC is often preferred). IC can be held in both calcite and dolomite which have slightly different VNIR absorptions

(Clark, 1999). SOC is comprised of a great variety of biomolecules, detritus, and humic substances. Extractable Fe is operationally defined (Mehra and Jackson, 1960), and we would probably be more interested in the amounts of soil hematite and goethite. Alternatively, we might want to build calibration models to predict soil composition directly—the types and amounts of minerals and organic molecules—rather than properties related to soil composition.

4.3. Auxiliary predictors

Sand content and pH (CaCl$_2$) both proved to be valuable auxiliary predictors. These soil properties (i) are simple and inexpensive to obtain; (ii) are fundamental soil characteristics; (iii) cannot be reliably related to VNIR-DRS; and (iv) improve the predictions of other soil properties. In certain regions, such as where silt is not an important soil component, this might not be as necessary or valuable. But given the difficulty in distinguishing between sand-and silt-sized quartz and feldspars with weak spectral signatures (Clark et al., 2003), sand vs. silt content might always be difficult to ascertain in temperate climates—even with larger or local calibration. Soil pH will only be related to VNIR-DRS to the extent that pH is related to soil constituent composition like SOC, IC and mineralogy. For many applications, this will not be sufficient. VNIR spectroscopy alone will never provide complete soil characterization, so application in parallel with other sensing technologies should be a focus of future research.

4.4. Calibration requirements

A key requirement for empirical modeling is that validation samples be similar to calibration samples (Shenk and Westerhaus, 1991a,b; Dardenne et al., 2000). Or, put another way, to build a global empirical VNIR-DRS soil characterization model we would need a calibration library that spanned the range of possibilities for soil composition. Following Dardenne et al. (2000) we constructed two theoretical soil composition models based on simple combinatorics, one global and another for highly weathered tropical soils (Table 8). We made a number of simplifying assumptions for our soil models, including most importantly (i) discrete constituent intervals of 5% are of suffi-

Table 8
Estimation of required calibration samples for empirical VNIR-DRS soil characterization, assuming (i) adequate span of compositional space can be accomplished with soil materials in units of 5%; (ii) all of the important soil materials are included below; and (iii) SOM, amphiboles, andic materials, etc... can be considered homogenous end member materials

Material	Global soil composition model (%)	Weathered soil composition model (%)
Amphiboles	0, 5, 10,..., 20	–
Andic materials	0, 5, 10,..., 100	–
Biotite	0, 5, 10,..., 25	–
Calcite	0, 5, 10,..., 20	–
Dolomite	0, 5, 10,..., 20	–
Gibbsite	0, 5, 10,..., 50	0, 5, 10,..., 50
Goethite	0, 5, 10,..., 40	0, 5, 10,..., 40
Hematite	0, 5, 10,..., 25	0, 5, 10,..., 25
Illite	0, 5, 10,..., 50	–
Kaolinite	0, 5, 10,..., 80	0, 5, 10,..., 80
Montmorillonite	0, 5, 10,..., 80	0, 5, 10,..., 20
Muscovite	0, 5, 10,..., 25	–
Olivine	0, 5, 10,..., 20	–
Pyroxenes	0, 5, 10,..., 20	–
Quartz and feldspars	0, 5, 10,..., 100	0, 5, 10,..., 100
Soil organic matter	0, 5, 10,..., 20	0, 5, 10
Vermiculite	0, 5, 10,..., 80	–
No. of combinations (required calibration)	5.2×10^9	5.9×10^4

ciently high resolution for the purposes of VNIR-DRS modeling; (ii) soil organic matter and "andic materials" are spectrally and compositionally homogenous; (iii) the minerals and mineral classes listed can be treated as single constituent end-members.

Despite these simplifying assumptions, we computed that 5.2×10^9 carefully selected calibration samples would be required to span the global soil compositional space. We computed a far more reasonable calibration size for our tropical soil model, 5.9×10^4 samples. Tropical soils are, on the whole, compositionally much less diverse than less weathered temperate soils and should therefore be more amenable to empirical modeling approaches. In regions with uniform parent material (e.g., loess deposits), we might also expect to construct reliable calibrations with a limited number of samples. Further research is needed to test whether local calibration procedures (Berzaghi et al., 2000) could help to reduce the size of calibration sets for regional or watershed applications. However, parent materials like glacial till with a range of primary and

secondary minerals might well require large calibration datasets even in geographically restricted areas.

Given the computed calibration requirements for a global soil characterization model, the results reported in this study show a remarkable level of accuracy and explanation. This suggests that (i) spectral absorptions of important soil materials are at least partially independent; (ii) viable empirical calibrations might be constructed with very large-but obtainable-soil spectral libraries on the order of 10^4 to 10^5 samples; and (iii) some soil properties, like the montmorillonite and kaolinite mineralogy reported in this study, might be reliably estimated with far fewer samples. Reliable calibrations for materials like wheat grains and forages can be constructed with just a few thousand samples (Shenk and Westerhaus, 1991a,b; Dardenne et al., 2000) but these materials are compositionally constrained by plant genetics. Soil composition is, unfortunately, not so constrained which makes the problem of VNIR-DRS soil characterization both different and more challenging than that of grain or forage analysis.

4.5. Future development

At present, with a relatively limited soil spectral library, we anticipate needing to refine predictions through four complementary approaches (Fig. 5).

- Expand the soil-spectral library by at least one order of magnitude by scanning previously characterized state and national soil archives. This work,

necessarily involving multiple labs, will require that we address calibration transfer between spectrometers of the same and different types.
- Augment the global library with local or regional calibration samples for local or regional prediction. In previous work by the lead author (Brown et al., in press), up to 30% calibration was required to obtain reliable SOC and IC predictions for glacial till soils in northern Montana. By using a global library in conjunction with local calibration, we anticipate both lowering calibration requirements and improving model robustness.
- Employ auxiliary predictors like sand content and pH, either measured in the lab or obtained through the use of complementary in situ sensors. For example, the complementary use of VNIR and Mid-Infrared (MIR) sensors (Janik et al., 1998) might overcome the limitations of each technology.
- A great deal more work is required to incorporate theoretical VNIR spectroscopy into soil DRS modeling. Uniform predictor transformations (e.g., log, $1/x$, x^2) will not improve BRT models, but local transformations like continuum-removal will lead to different predictions. Using these techniques to isolate spectral features can be used in conjunction with high-dimensional quantitative techniques like BRT or in expert systems like Tetracoder (Clark et al., 2003).

5. Conclusions

In this VNIR-DRS study of 4184 largely independent samples from the U.S. Soil Survey archives, we found strong relationships between VNIR reflectance and the following important soil properties: relative kaolinite content, relative montmorillonite content, clay content (pipette), CEC (NH_4 at pH=7), SOC (Walkley–Black), IC (HCl with electronic manometer) and citrate–dithionite extractable Fe. Given the broad sampling across the United States, the Americas, Africa and Asia, this demonstrates the fundamental viability of VNIR-DRS for global soil characterization. The fact that information on a number of fundamental soil properties can be obtained simultaneously provides promise for the use of VNIR-DRS in many practical agronomic and environmental applications, including the development and monitoring of soil health indicators.
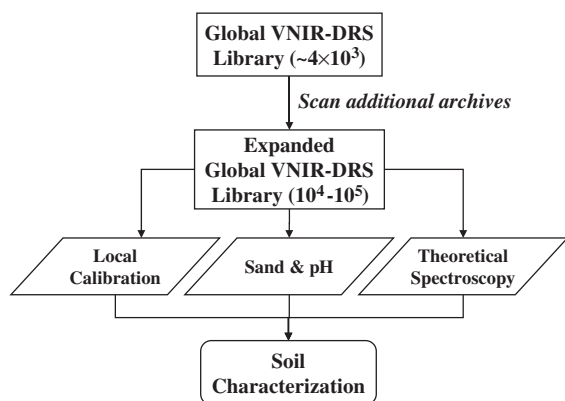

Fig. 5. Schematic diagram of proposed process to obtain reliable, robust and accurate estimates of local soil properties using VNIR-DRS.

Given the compositional diversity of soils, we estimate that on the order of 10^9 independent samples would be required to construct a *complete* global, empirical soil library for calibration purposes. However, since we were able to construct useful predictive models with just 3000–4000 samples in this study, fundamental and partially independent soil-spectral relationships may reduce the required number of calibration samples to a manageable number (perhaps 10^4–10^5). For highly weathered tropical soils with limited mineralogical diversity empirical calibrations should be obtainable with far fewer samples. In the interim, at least for temperate regions, we propose that global libraries be used in conjunction with local calibration samples and with easy-to-measure auxiliary predictors like sand content and pH. Developments in theoretical soil spectroscopy and spectral processing techniques should also improve predictions while reducing calibration requirements.

Boosted regression trees (BRT) proved far superior to PLS regression and have many desirable qualities such as (i) the ability to model interactions and non-linear relationships; (ii) relative immunity to overfitting; and (iii) the ability to utilize a large number of "weak classifiers" and thereby make maximum use of the entire VNIR spectrum.

The protection and enhancement of the global environment requires the development of innovative new methodologies to assess the spatial and temporal variability of soil properties. In particular, spectroscopic techniques like Visible and Near-Infrared Diffuse Reflectance Spectroscopy (VNIR-DRS) offer the potential to quickly and inexpensively characterize soils relative to standard laboratory techniques. We anticipate that the future development of VNIR soil spectroscopy and the expansion of soil-spectral libraries will support the assessment of soil variability at a scale and resolution not previously possible.

Acknowledgements

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